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Request for grant of a patent

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1.	Your Reference	APB/GRK/Q210
2.	Application number	**9913572.5**
3.	Full name, address and postcode of the or each Applicant Country/state of incorporation (if applicable)	Victrex Manufacturing Ltd. Victrex Technology Centre Hillhouse International PO Box 4 THORNTON CLEVELEYS Lancashire FY5 4QD 6510887001 Incorporated in: UK
4.	Title of the invention	SULPHONATED POLYARYLETHERKETONES
5.	Name of agent Address for service in the UK to which all correspondence should be sent Patents ADP number	APPLEYARD LEES 15 CLARE ROAD HALIFAX HX1 2HY AA005 190001

6. Priority claimed to:

Country	Application number	Date of filing
United Kingdom	9819706.4	11 Sep 1998
United Kingdom	9820940.6	28 Sep 1998

7. Divisional status claimed from:

Number of parent application	Date of filing
-	-

8. Is a statement of inventorship and of right to grant a patent required in support of this application? YES

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document	
Continuation sheets of this form	—
Description	36 /
Claim(s)	— 8
Abstract	—
Drawing(s)	1 /
10. If you are also filing any of the following, state how many against each item	
Priority documents	
Translation of priority documents	
Statement of inventorship and right to grant a patent (PF 7/77)	
Request for a preliminary examination and search (PF 9/77)	
Request for substantive examination (PF 10/77)	
Any other documents (please specify)	
11.	We request the grant of a patent on the basis of this application. Signature: APPLEYARD LEES (signed: Appleyard Lees) Date: 11 June 1999
12. Contact	**Anthony P Brierley** **01422 330110**

SULPHONATED POLYMERS

This invention relates to sulphonated polymers and particularly, although not exclusively, relates to sulphonated polyaryletherketones, polyarylethersulphones and/or copolymers of the aforesaid. Preferred embodiments of the invention relate to ion-conductive membranes, for example of polymer electrolyte membrane fuel cells, made using such polymers. The invention also relates to novel non-sulphonated polyaryletherketones and/or polyarylethersulphones used for preparing said sulphonated polymers and processes for the preparation of polymers described herein.

A polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

In a PEMFC, hydrogen is introduced at the anode (fuel electrode) which results in the following electrochemical reaction:

Pt-Anode (Fuel Electrode) $2H_2 \rightarrow 4H^+ + 4e^-$

The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following electrochemical reaction takes place:

Pt-Cathode (Oxidant Electrode) $O_2 + 4H^+ = 4e^- \rightarrow 2H_2O$

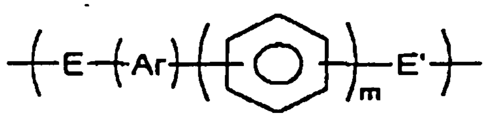
Thus, electrons and protons are consumed to produce water and heat. Connecting the two electrodes through an external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.

US Patent No. 5 561 202 (Hoechst) discloses the production of PEMs from sulphonated aromatic polyether ketones. At least 5% of the sulphonic groups in the sulphonic acid moieties are converted into sulphonyl chloride groups and then reacted with an amine containing at least one cross-linkable substituent or a further functional group. An aromatic sulphonamide is then isolated, dissolved in an organic solvent, converted into a film and then the cross-linkable substituents in the film are cross-linked. The invention is said to provide ion-conductive membranes suitable for use as polymeric solid electrolytes which have adequate chemical stability and can be produced from polymers which are soluble in suitable solvents.

One problem associated with known PEMFCs is that of providing PEMs which have desirable properties at elevated temperatures and which are cheap to manufacture.

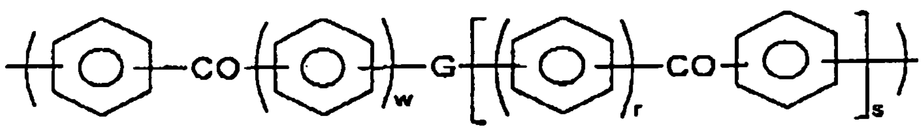
It is an object of the present invention to address problems associated with PEMs.

According to a first aspect of the invention, there is provided a polymer electrolyte membrane which includes a polymer having a moiety of formula



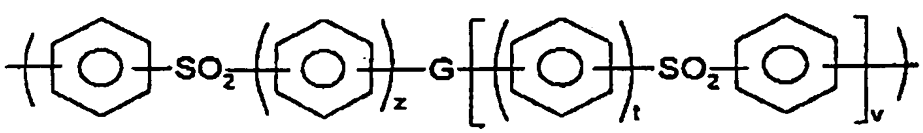
I

and/or a moiety of formula



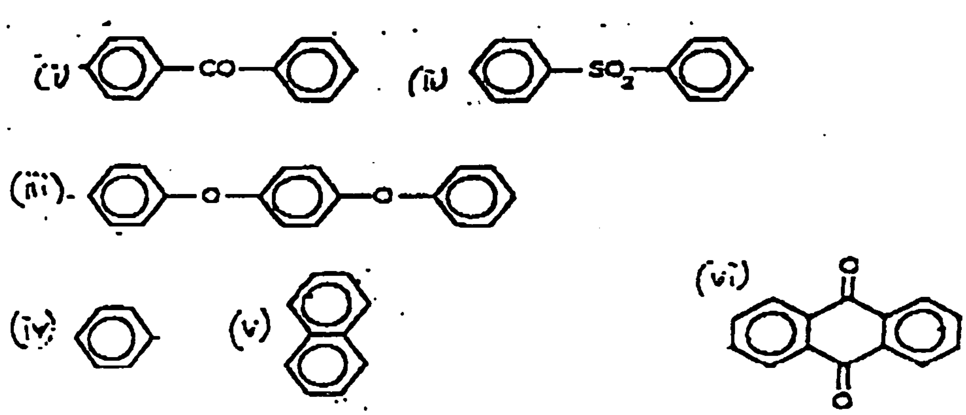
II

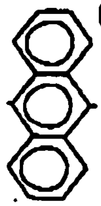
and/or a moiety of formula

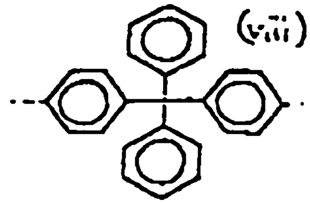


III

wherein at least some of the units I, II and/or III are sulphonated; wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and wherein m,r,s,t,v,w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from one of the following moieties (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties




(vii)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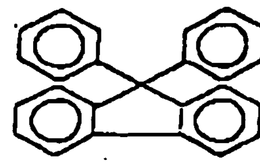
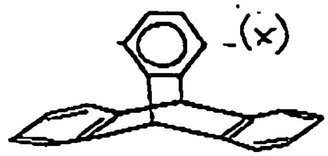

(ix)


(x)

Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

Said polymer may include more than one different type of repeat unit of formula I; more than one different type of repeat unit of formula II; and more than one different type of repeat unit of formula III.

Where the phenyl moieties in units I, II or III are optionally substituted, they may be optionally substituted by one or more halogen, especially fluorine and chlorine, atoms or alkyl, cycloalkyl or phenyl groups. Preferred alkyl groups are C_{1-10}, especially C_{1-4}, alkyl groups. Preferred cycloalkyl groups include cyclohexyl and multicyclic groups, for example adamantyl. In some cases, the optional substituents may be used in the cross-linking of the polymer. For example, hydrocarbon optional substituents may be functionalised, for example sulphonated, to allow a cross-linking reaction to tak place. Preferably, said phenyl moieties are unsubstituted.

Where said polymer is cross-linked, it is suitably cross-linked so as to improve its properties as a polymer electrolyte membrane, for example to reduce its

swellability in water. Any suitable means may be used to effect cross-linking. For example, where E represents a sulphur atom, cross-linking between polymer chains may be effected via sulphur atoms on respective chains. Alternatively, said polymer may be cross-linked via sulphonamide bridges as described in US 5 561 202. A further alternative is to effect cross-linking as described in EP-A-0008895.

However, for polymers according to the first aspect which are crystalline (which some are) there may be no need to effect cross-linking to produce a material which can be used as a polymer electrolyte membrane. Such polymers may be easier to prepare than cross-linked polymers. Thus, said polymer of the first aspect is preferably crystalline. Preferably, said polymer is not optionally cross-linked as described.

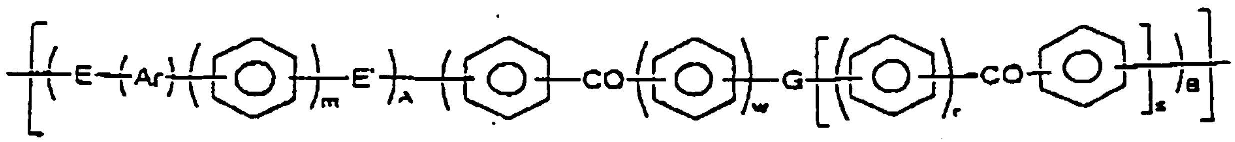
Where w and/or z is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene moieties have 1,4- linkages.

Preferably, G represents a direct link.

Suitably, "a" represents the mole % of units of formula I in said polymer; "b" represents the mole % of units of formula II in said polymer; and "c" represents the mole % of units of formula III in said polymer. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52. Preferably, the sum of b and c is in the range 0-55, more preferably in the range

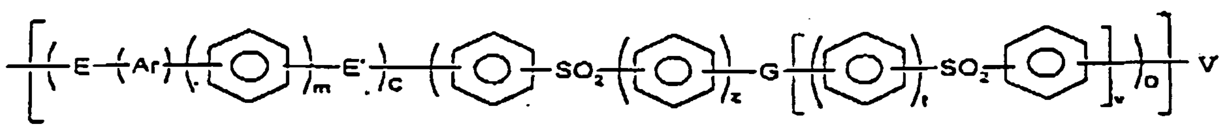
45-55, especially in the range 48-52. Preferably, the sum of a, b and c is 100.

Said polymer may be a homopolymer having a repeat unit of general formula



IV

or a homopolymer having a repeat unit of general formula



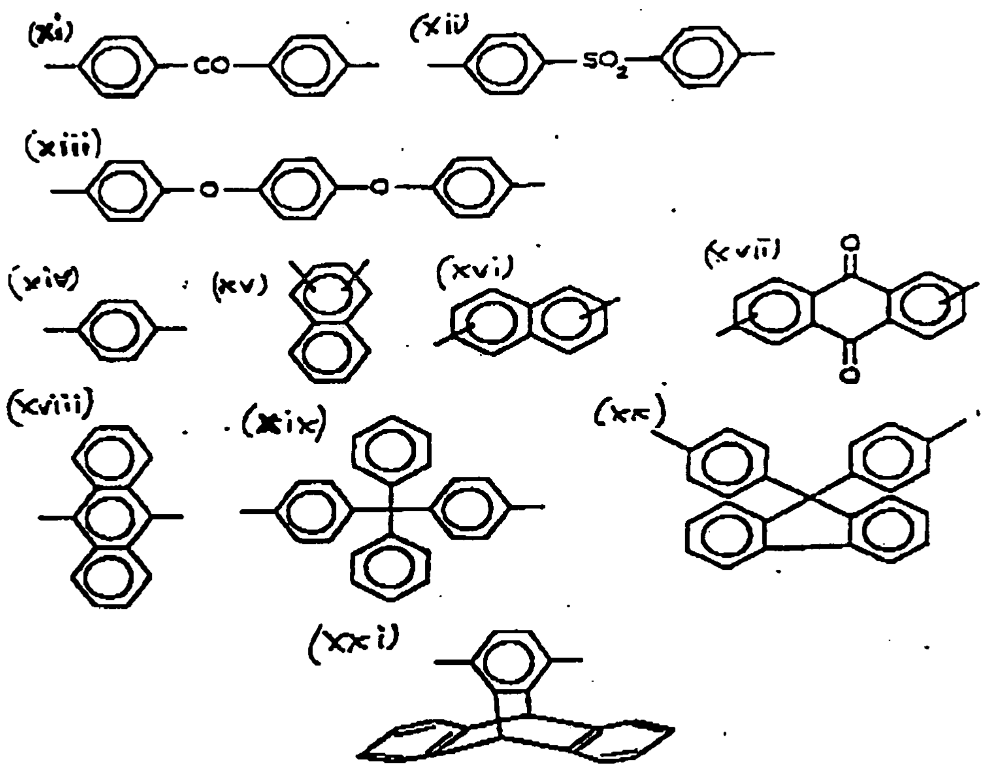
V

or a random or block copolymer of at least two different units of IV and/or V

wherein A, B, C and D independently represent 0 or 1 and E,E',G,Ar,m,r,s,t,v,w and z are as described in any statement herein.

Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, s is 0 or 1. Preferably v is 0 or 1. Preferably, w is 0 or 1. Preferably z is 0 or 1.

Preferably Ar is selected from the following moieties (xi) to (xxi):



Preferably, (xv) is selected from a 1,2-, 1,3-, or a 1,5- moiety; (xvi) is selected from a 1,6-, 2,3-, 2,6- or a 2,7- moiety; and (xvii) is selected from a 1,2-, 1,4-, 1,5-, 1,8- or a 2,6- moiety.

Referring to formula IV, preferably, said polymer is not a polymer wherein: Ar represents moiety (iv), E and E' represent oxygen atoms, m represents zero, w represents 1, s represents zero, and A and B represent 1; Ar represents

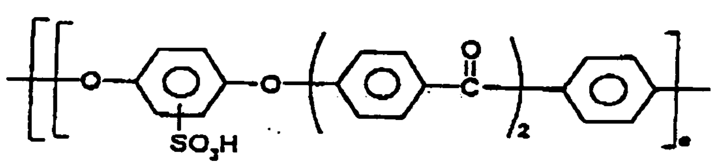
moiety (i), E and E' represent oxygen atoms, G represents a direct link, m represents zero, w represents 1, r represents 0, s represents 1 and A and B represent 1; Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents 0, w represents 0, s represents 1, r represents 1 and A and B represent 1. Referring to formula V, preferably Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents zero, z represents 1, v represents zero and C and D represent 1.

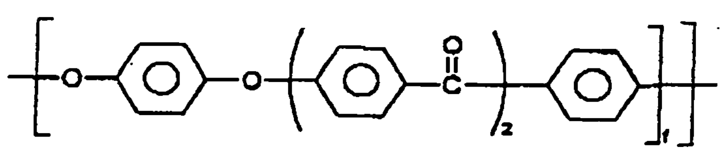
Preferably, said polymer is not a sulphonated aromatic polyetherketone of formula

$$-[[Ph-O]_p-Ph-[[CO-Ph']_x-O-Ph]_h-[CO-Ph']_y-[O-Ph]_n-CO-]-$$

where Ph represents a 1,4- or 1,3- phenylene moiety; Ph' represents phenylene, naphthylene, biphenylene or anthrylene; p is 1, 2, 3 or 4; x, h and n are, independently, zero or 1; and y is 1, 2 or 3.

Preferably, said polymer does not conform to the formula

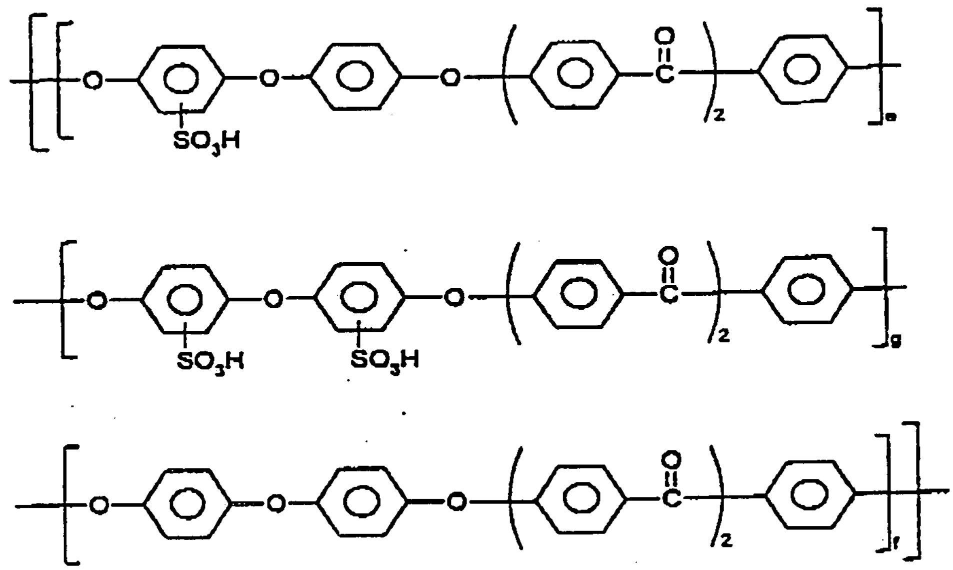




where

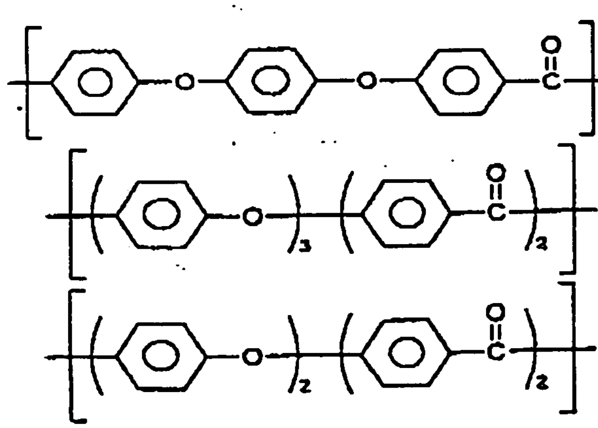
e is from 0.2 to 1,
f is from 0 to 0.8, and
e + f = 1

Preferably, said polymer does not conform to the formula



in which e is a number from 0 to 1, g is a number from 0 to 1, f is a number from 0 to 0.5, and the sum e + f + g = 1.

Preferably, said polymer is not a copolymer built up from at least two different units of formulae:



Preferred moieties Ar are moieties (i), (ii) and (iv), especially moieties (xi), (xii) and (xiv).

Preferred polymers include a biphenylene moiety. Preferred polymers include a -O-biphenylene-O- moiety.

Preferred polymers include a first type of moiety which is relatively difficult to sulphonate and a second type of moiety which is relatively easy to sulphonate. For example, said second moiety may be sulphonatable using the relatively mild method described in Example 10 hereinafter, whereas the first moiety may be substantially non-sulphonatable in such a method. The use of the method of Example 10 may be advantageous over currently used methods which use oleum. A preferred second said moiety includes a moiety $-Ph_n-$ wherein n is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen. Especially preferred is the case wherein said moiety is $-O-Ph_n-O-$ where said ether groups are para to the Ph-Ph bond.

Preferred polymers are copolymers comprising a first repeat unit which is selected from the following:

(a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1;

(b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

(c) a unit of formula V wherein E and E^1 represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

(d) a unit of formula V wherein E represents an oxygen atom, E^1 represents a direct link, Ar represents a moiety of structure (i), m represents 0, C represents 1, D represents 0; or

(e) a unit of formula V wherein E and E^1 represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents O and D represents 1;

and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1;

(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

(h) a unit of formula V wherein E and E^1 represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

(i) a unit of formula V wherein E represents an oxygen atom, E^1 represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

More preferred polymers are copolymers having a first repeat unit selected from those described above, especially repeat units (b), (d) or (e) in combination with a second repeat unit selected from units (f) or (h).

Copolymers may be prepared having one or more first repeat units and one or more of said second repeat units.

Where said polymer is a copolymer as described, the mole% of co-monomer units, for example said first and second repeat units described above, may be varied to vary the solubility of the polymer in solvents, for example in organic solvents which may be used in the preparation of films and/or membranes from the polymers and/or in other solvents, especially water.

Preferred polymers have a solubility in the range 10 to 30 %w/v in a polar aprotic solvent, for example NMP, DMSO or DMF. Preferred polymers are substantially insoluble in boiling water.

First units of the type described above (with the exception of units (a) and (c)) may be relatively difficult to sulphonate, whereas second units of the type described may be easier to sulphonate.

Where a phenyl moiety is sulphonated, it may only be mono-sulphonated.

In general terms, where a said polymer includes a -O-phenyl-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. Where a said polymer includes a -O-biphenylene-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. It is believed to be possible to sulphonate relatively easily -O-(phenyl)$_n$-O- moieties wherein n is an integer, suitably 1-3, at up to 100 mole%. Moieties of formula -O-(phenyl)$_n$-CO- or -O-(phenyl)$_n$-SO_2- may also be sulphonated at up to 100 mole% but more vigorous conditions may be required. Moieties of formulae -CO-(phenyl)$_n$-CO- and -SO_2-(phenyl)$_n$-SO_2- are more more difficult to sulphonate and may be sulphonated to a level less than 100 mole% or not at all under some sulphonation conditions.

The glass transition temperature (T_g) of said polymer may be at least 154°C, suitably at least 160°C, preferably at least 164°C, more preferably at least 170°C, especially at least 190°C. In some cases, the Tg may be greater than 250°C or even 300°C.

Said polymer may have an inherent viscosity (IV) of at least 0.3, suitably at least 0.4, preferably at least 0.7 (which corresponds to a reduced viscosity (RV) of least 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84gcm^{-3}, said solution containing 1g of polymer per 100cm^{-3} of solution. IV is measured at 25°C on a solution of polymer in concentrated sulphuric acid of density 1.84gcm^3, said solution containing 0.1g of polymer per 100cm^3 of solution.

The measurements of both RV and IV both suitably employ a viscometer having a solvent flow time of approximately 2 minutes.

In general terms, said polymer is preferably substantially stable when used as a PEM in a fuel cell. Thus, it suitably has high resistance to oxidation, reduction and hydrolysis and has very low permeability to reactants in the fuel cell. Preferably, however, it has a high proton conductivity. Furthermore, it suitably has high mechanical strength and is capable of being bonded to other components which make up a membrane electrode assembly.

Said polymer may comprise a film, suitably having a thickness of less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05 mm. The film may have a thickness of at least 5μm.

The polymer electrolyte membrane suitably includes a layer of a catalyst material, which may be a platinum catalyst or a mixture of platinum and ruthenium, on both sides of the polymer film. Electrodes may be provided outside the catalyst material.

It is believed that polymers which include phenyl groups which are not deactivated (i.e. which do not have electron withdrawing groups attached) may be more susceptible to attack, in use, by .OH or .OOH radicals and, consequently, the lifetime of membranes produced from such polymers may be reduced. Phenyl groups deactivated by sulphone groups may be less susceptible to attack compared to phenyl groups deactivated by ketone groups. Thus,

polyarylethersulphone polymers may be more stable to radical attack compared to polyaryletherketone - polyarylethersulphone copolymers which, in turn, may be more stable than polyaryletherketone polymers. It may be preferable for each phenyl group in a sulphonated polymer as described to be deactivated by being bonded directly to an electron withdrawing group, for example a sulphonated group, a sulphone group or a ketone group.

According to a second aspect of the invention, there is provided a polymer electrolyte membrane which includes a polymer which includes: polyaryletherketone and/or polyarylethersulphone units; and units of formula $-O-Ph_n-O-$ (XX) wherein Ph represents a phenyl group and n represents an integer of 2 or greater and wherein Ph groups of units (XX) are sulphonated.

Preferably, each phenyl group of moiety Ph_n is sulphonated, preferably mono-sulphonated. About 100 mole% of such phenyl groups may be sulphonated as described.

Preferably, $-OPhCO-$ and/or $-OPhSO_2-$ moieties of said polymer are sulphonated to a lesser extent than the phenyl groups of moiety Ph_n. Moieties $-OPhCO-$ and $-OPhSO_2-$ may be substantially non-sulphonated.

In one embodiment, said polymer may include no ketone linkages and may have an equivalent weight of more than 900. Nonetheless, it has been found, surprisingly, that such polymers are still conducting.

Said polymer electrolyte membrane may be for a fuel cell or an electrolyser.

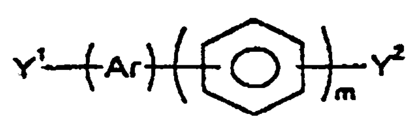
The invention extends to the use of a polymer which includes relatively easy to sulphonate units and relatively difficult to sulphonate units in the preparation of a polymer for a polymer electrolyte membrane.

According to a third aspect of the invention, there is provided a fuel cell or an electrolyser (especially a fuel cell) incorporating a polymer electrolyte membrane according to the first or second aspects.

According to a fourth aspect of the invention, there is provided any novel polymer as described according to said first aspect <u>per se</u>.

According to a fifth aspect of the invention, there is provided a process for the preparation of a polymer as described in the first, second, third and/or fourth aspects, the process comprising:

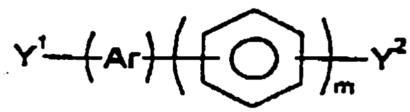
(a) polycondensing a compound of general formula



VI

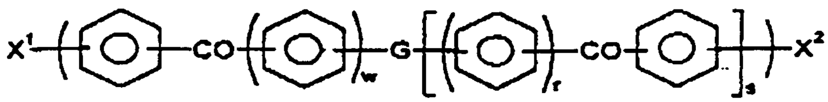
with itself wherein Y^1 represents a halogen atom or a group -EH and Y^2 represents a halogen atom or, if Y^1 represents a halogen atom, Y^2 represents a group E'H; or

(b) polycondensing a compound of general formula



VI

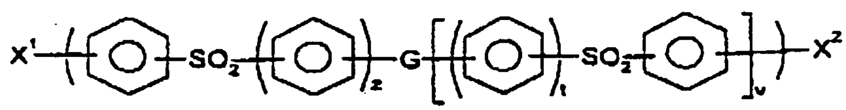
with a compound of formula



VII

and/or with a compound of formula

VIII



wherein Y^1 represents a halogen atom or a group -EH (or -E'H if appropriate) and X^1 represents the other one of a halogen atom or group -EH(or -E'H if appropriate) and Y^2 represents a halogen atom or a group -E'H and X^2 represents the other one of a halogen atom or a group -E'H (or -EH if appropriate).

(c) optionally copolymerizing a product of a process as described in paragraph (a) with a product of a process as described in paragraph (b);

wherein the phenyl moieties of units VI, VII and/or VIII are optionally substituted; the compounds VI, VII and/or VIII are optionally sulphonated; and Ar, m, w, r, s, z, t, v, G, E and E' are as described above except that E and E' do not represent a direct link;

the process also optionally comprising sulphonating and/or cross-linking a product of the reaction described in paragraphs (a), (b) and/or (c) to prepare said polymer.

Preferably, where Y^1, Y^2, X^1 and/or X^2 represent a halogen, especially a fluorine, atom, an activating group, especially a carbonyl or sulphone group, is arranged ortho- or para- to the halogen atom.

Advantageously, where it is desired to prepare a copolymer comprising a first repeat unit IV or V wherein E represent an oxygen or sulphur atom, Ar represents a moiety of structure (i), m represents zero, E' represents a direct link, A represents 1 and B represents zero and a second repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m and w represent 1, G represents a direct link, s represents zero and A and B represent 1 wherein the polymer is not a random polymer but has a regular structure, the process described in paragraph (b) above may be used wherein in said compound of general formula VI, Y^1 and Y^2 represent -OH or -SH groups, Ar represents a moiety of structure (iv) and m represents 1 and in said compounds of general formulae VII and VIII, X^1 and X^2 represent a fluorine atom, w,r,s,z,t and v represent 1 and G represents an oxygen or sulphur atom.

In another embodiment, where it is desired to prepare a copolymer comprising a first repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m represents zero, A represents 1, w represents 1, s represents zero and B represents 1 and

a second repeat unit IV or V wherein E and E' represent an oxygen or sulphur atom, Ar represents a moiety of structure (iv), m and w represent 1, s represents zero and A and B represent 1, wherein the polymer is not a random polymer but has a regular structure, the process described in paragraph (b) above may be used wherein in said compound of general formula VI, Y^1 and Y^2 represent -OH or -SH groups, Ar represents a moiety of structure (iv) and m represents 1 and in said compounds of general formulae VII and VIII, X^1 and X^2 represent a fluorine atom, w,r,s,z,t and v represent 1 and G represents a -O-Ph-O- moiety.

Preferred halogen atoms are fluorine and chlorine atoms, with fluorine atoms being especially preferred. Preferably, halogen atoms are arranged meta- or para- to activating groups, especially carbonyl groups.

Where the process described in paragraph (a) is carried out, preferably one of Y^1 and Y^2 represents a fluorine atom and the other represents an hydroxy group. More preferably in this case, Y^1 represents a fluorine atom and Y^2 represents an hydroxy group. Advantageously, the process described in paragraph (a) may be used when Ar represents a moiety of structure (i) and m represents 1.

When a process described in paragraph (b) is carried out, preferably, Y^1 and Y^2 each represent an hydroxy group. Preferably, X^1 and X^2 each represent a halogen atom, suitably the same halogen atom.

Compounds of general formula VI, VII and VIII are commercially available (eg from Aldrich U.K.) and/or may be prepared by standard techniques, generally involving

Friedel-Crafts reactions, followed by appropriate derivatisation of functional groups. The preparations of some of the monomers described herein are described in P M Hergenrother, B J Jensen and S J Havens, Polymer 29, 358 (1988), H R Kricheldorf and U Delius, Macromolecules 22, 517 (1989) and P A Staniland, Bull, Soc, Chem, Belg., 98 (9-10), 667 (1989).

Where compounds VI, VII and/or VIII are sulphonated, compounds of formulas VI, VII and/or VIII which are not sulphonated may be prepared and such compounds may be sulphonated prior to said polycondensation reaction.

Sulphonation as described herein may be carried out in concentrated sulphuric acid (96%w/w) at an elevated temperature. For example, dried polymer may be contacted with sulphuric acid and heated with stirring at a temperature of greater than 40°C, preferably greater than 55°C, for at least one hour, preferably at least two hours, more preferably about three hours. The desired product may be caused to precipitate, suitably by contact with cooled water, and isolated by standard techniques. Sulphonation may also be effected as described in US5362836 and/or EP0041780.

Where the process described in paragraph (b) is carried out, suitably, "a*" represents the mole% of compound VI used in the process; "b*" represents the mole % of compound VII used in the process; and "c*" represents the mole % of compound VIII used in the process.

Preferably, a* is in the range 45-55, especially in the range 48-52. Preferably, the sum of b* and c* is in the

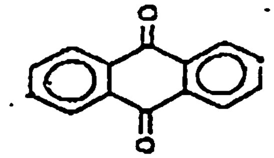
range 45-55, especially in the range 48-52. Preferably, the sum of a*, b* and c* is 100.

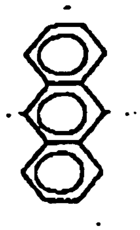
Where the process described in paragraph (b) is carried out, preferably, one of either the total mole % of halogen atoms or groups -EH/-E'H in compounds VI, VII and VIII is greater, for example by up to 10%, especially up to 5%, than the total mole % of the other one of either the total mole % of halogen atoms or groups -EH/-E'H in compounds VI, VII and VIII. Where the mole % of halogen atoms is greater, the polymer may have halogen end groups and be more stable than when the mole % of groups -EH/-E'H is greater in which case the polymer will have -EH/-E'H end groups. However, polymers having -EH/-E'H end groups may be advantageously cross-linked.

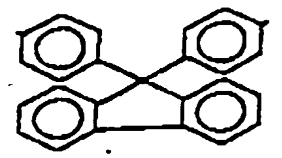
It is believed that certain polymers described herein are novel and, therefore, in a sixth aspect, the invention extends to any novel polymer described herein per se.

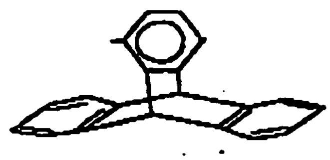
It is also believed that certain polymers according to said first and/or second aspect but which are not sulphonated are novel. Thus, according to a seventh aspect of the invention, there is provided a novel polymer having a moiety of formula I and/or a moiety of formula II and/or a moiety of formula III wherein E,E',G,m,r,s,t,v,w,z and Ar are as described in any statement herein.

Preferably, said polymer includes a moiety of formula II and/or III and Ar is selected from









Preferably, in the aforementioned formulae, each -Ar- is bonded to adjacent moieties as described in any statement herein.

According to an eighth aspect of the invention, there is provided a process for the preparation of novel polymers according to said seventh aspect, the process being as described according to the process of the fifth aspect except that compounds VI, VII and VIII are not sulphonated and the process does not include a sulphonation step.

Sulphonated polymers described herein may be made into films and/or membranes for use as PEMs by conventional techniques, for example as described in Examples 5 to 7 of US 5561202.

The sulphonated polymers described herein may be used as polymer electrolyte membranes in fuel cells or electrolysers as described. Additionally, they may be used as gas diffusion electrodes.

Any feature of any aspect of any invention or example described herein may be combined with any feature of any aspect of any other invention or example described herein.

Specific embodiments of the invention will now be described, by way of example, with reference to figure 1 which is a schematic representation of a polymer electrolyte membrane fuel cell.

As described above, the fuel cell includes a thin sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane. The preparation of sheet material for such a membrane is described hereinafter.

Example 1

A 500ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (35.79g, 0.164 mole), hydroquinone (11.01g, 0.10 mole), 4,4'-dihydroxybiphenyl (18.62g, 0.10 mole), 4,4'-bis(4-chlorophenylsulphonyl)biphenyl (LCDC)(20.13g, 0.04 mole) and diphenylsulphone (202.76g) and the contents were heated under a nitrogen blanket to 160°C to form a nearly colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (29.02g, 0.21 mole) was added and the mixture stirred for 35 minutes. The temperature was raised gradually to 220°C over 2 hours then raised to 280°C over 2 hours and maintained for 2 hours.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer

had a reduced viscosity of (RV) 2.50 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm^{-3}, said solution containing 1g of polymer/100cm^3) and a Tg of 186°C.

Example 2

A 250ml, 3-necked round-bottomed flask fitted with stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (33.06g, 0.1515 mole), hydroquinone (13.21g, 0.12 mole), 9,9'-bis(4-hydroxyphenyl)fluorene(HPF) (10.512g, 0.03 mole), and diphenylsulphone (100.93g) and the contents were heated under a nitrogen blanket to 150°C to form a nearly colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (21.77g, 0.15751 mole) was added. The temperature was raised to 175°C maintained for 2 hours, raised to 200°C maintained for 50 minutes, raised to 250°C maintained for 45 minutes, raised to 300°C maintained for 90 minutes.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had an reduced viscosity (RV) of 0.76 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm^{-3}, said solution containing 1g of polymer/100cm^3) and a Tg of 165°C.

Example 3

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with

4,4'-difluorobenzophenone (11.36g, 0.052 mole), 4,4'-dihydroxybenzophenone (21.42g, 0.10 mole), LCDC (25.72g, 0.05 mole), and diphenylsulphone (90g) and the contents were heated under a nitrogen blanket to 155°C to form a nearly colourless solution. While maintaining a nitrogen blanket, anhydrous sodium carbonate (10.60g, 0.10 mole) and potassium carbonate (0.28g, 0.002 mole) was added. The temperature was raised to 180°C and maintained for 20 minutes, raised to 200°C and maintained for 1 hour, raised to 250°C and maintained for 30 minutes, raised to 275°C and maintained for 20 minutes, raised to 300°C and maintained for 20 minutes, raised to 325°C and maintained for 2 hours.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had a Tg of 200°C.

Example 4

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-bis(4-chlorophenylsulphonyl)-terphenyl (23.2g, 0.04 mole), 4,4'-dihydroxybiphenyl (7.44g, 0.040 mole) and diphenylsulphone (80g) and the contents were heated under a nitrogen blanket to 170°C to form a nearly colourless solution. While maintaining a nitrogen blanket, anhydrous potassium carbonate (5.64g, 0.408 mole) was added. The temperature was raised to 200°C and maintained for 30 minutes, raised to 250°C and maintained for 15 minutes, raised to 275°C and maintained for 15 minutes, raised to 330°C and maintained for 1 hour.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had an inherent viscosity (IV) of 0.50 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm^{-3}, said solution containing 0.1g of polymer/100cm^3) and a Tg of 264°C.

Example 5

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (21.82g, 0.10 mole), 4,4'-dihydroxybiphenyl (18.62g, 0.10 mole) and diphenylsulphone (60g) and the contents were heated under a nitrogen blanket to 180°C to form a nearly colourless solution. While maintaining a nitrogen blanket anhydrous potassium carbonate (14.10g, 0.102 mole) was added. The temperature was raised to 200°C over 60 minutes, raised to 250°C maintained for 5 mins, raised to 325°C maintained for 5 mins, raised to 370°C over 90 mins, maintained for 10 mins.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had an inherent viscosity (RV) of 1.28 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm^{-3}, said solution containing 1g of polymer/100cm^3) and a Tg 167°C.

Example 6

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-difluorobenzophenone (22.04g, 0.101 mole), 4,4'-dihydroxybiphenyl (6.52g, 0.035 mole), hydroquinone (7.16g, 0.065 mole) and diphenylsulphone (60g) and the contents were heated under a nitrogen blanket to 180°C to form a nearly colourless solution. While maintaining a nitrogen blanket anhydrous sodium carbonate (10.60g, 0.100 mole) and anhydrous potassium carbonate (0.28g, 0.002 mole) were added. The temperature was raised to 200°C held for 1 hour, raised to 250°C held for 1 hour, raised to 300°C held for 1 hour. The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer has an inherent viscosity (IV) 0.92 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84 $g.cm^{-3}$, said solution containing 0.1 g of polymer/$100cm^3$) and a Tg 156°C.

Example 7

A 250ml, 3-necked round-bottomed flask fitted with a stirrer, nitrogen inlet and air condenser was charged with 4,4'-bis(4-fluorobenzoyl)diphenylether (21.34g, 0.515 mole), 4,4'-dihydroxybiphenyl (9.31g, 0.050 mole) and diphenylsulphone (90g) and the contents were heated under a nitrogen blanket to 160°C to form a nearly colourless solution. While maintaining a nitrogen blanket anhydrous sodium carbonate (5.30g, 0.050 mole) and anhydrous potassium carbonate (0.14g, 0.001 mole) were added. The

temperature was raised at 1°C/min until it reached 345°C and held for 1 hour.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol and water. The resulting solid polymer was dried at 140°C under vacuum. The polymer had an inherent viscosity (RV) 1.48 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density $1.84g.cm^{-3}$, said solution containing 1g of $polymer/100cm^3$) and a Tg 163°C.

Example 8 - General procedure for Sulphonation of Polymers of Examples 1 to 7

The polymers prepared as described in Examples 1 to 7 were sulphonated according to the following procedure.

The dried polymer was placed in a three-necked round-bottomed flask fitted with a stirrer containing 98% concentrated sulphuric acid ($100cm^3$), heated with stirring to 60°C and maintained at the temperature for 3 hours. The reaction product was poured into 5 litres of stirred ice/water mixture. The product precipitated out. It was then filtered-off, washed with iced-water until the pH was neutral, washed with methanol and dried under vacuum at 100°C. The degree of sulphonation was determined by elemental analysis, filtration or Nmr.

Example 9 - Sulphonation of polymer of Example 6 (Process 1)

The dried polymer from Example 6 (10g) was placed in a three-necked round-bottomed flask fitted with a stirrer,

containing 98% concentrated sulphuric acid ($100cm^3$), heated with stirring to 60°C and maintained at that temperature for 3 hours. The reaction products was poured into 5 litres of stirred ice/water mixture. The product precipitated out, was filtered-off, washed with iced-water until the pH was neutral, washed with methanol and dried under vacuum at 100°C. Nmr analysis showed the polymer had readily sulphonated, in which 95-100 mole% of the ether-diphenyl-ether and ether-phenyl-ether units had been sulphonated.

Example 10 - Sulphonation of polymer of Example 6 (Process 2)

The dried polymer from Example 6 (10g) was placed in a three-necked round-bottomed flask fitted with a stirrer, containing 96% concentrated sulphuric acid ($100cm^3$) and stirred for 90 minutes at 60°C until the polymer was completely dissolved. Oleum was added to bring the sulphuric acid concentration up to 98.5%. The mixture was heated with stirring to 80°C and maintained at that temperature for 3 hours. The reaction product was poured into 5 litres of stirred ice/water mixture. The product precipitated out, was filtered-off, washed with iced-water until the pH was neutral, washed with methanol and dried under vacuum at 100°C. Nmr analysis showed the polymer had readily sulphonated, in which 100 mole% of the ether-diphenyl-ether and ether-phenyl-ether units and 26 mole% of the ether-phenyl-ketone units had been sulphonated.

Example 11

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybenzophenone (34.28g, 0.16 mole), 4,4'-dihydroxybiphenyl (44.69g, 0.24 mole) and diphenysulphone (332g) and purged with nitrogen for at least 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 145°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (43.24g, 0.408 mole) was added. The temperature was raised gradually to 335°C over 200 minutes then maintained for 1 hour.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a Tg of 164°C, a melt viscosity at 400°C, 1000sec^{-1} of 0.48 $kNsm^{-2}$ and an inherent viscosity (IV) 0.40 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84$g.cm^{-3}$, said solution containing 0.1g of polymer/100cm^3).

Examples 12 to 15

The polymerisation procedure of Example 11 was followed, except that copolymers of different compositions were prepared by varying the mole ratios of 4,4'-dihydroxybenzophenone to 4,4'-dihydroxybiphenyl, with the sum of the number of moles of the aforesaid reactants equalling the number of moles of 4,4'-difluorobenzophenone, as described in Example 11. A

summary of the mole ratios and the MV are detailed in the table below.

Example No	4,4' dihydroxybiphenyl: 4,4'-dihydroxybenzophenone	MV(kNsm^{-2})
12	2:1	0.17
13a	1:1	0.48
13b (1)	1:1	0.69
14	1:2	0.54
15	1:3	0.43

(1) The polymerisation procedure of Example 11 was followed except dried sodium carbonate (43.24g, 0.408 mole) was replaced by dried sodium carbonate (42.44g, 0.4 mole) and dried potassium carbonate (1.11g, 0.008 mole).

Example 16a

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-difluorobenzophenone (89.03g, 0.408 mole), 4,4'-dihydroxybiphenyl (37.24g, 0.2 mole) 4,4'-dihydroxydiphenylsulphone (50.05g, 0.2 mole), and diphenysulphone (332g) and purged with nitrogen for over 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 150°C to form an almost colourless solution. While maintaining a nitrogen blanket, dried sodium carbonate (42.44g, 0.4 mole) and potassium carbonate (1.11g, 0.008 mole) were added. The temperature was raised gradually to 315°C over 3 hours then maintained for 0.5 hours.

The reaction mixture was allowed to cool, milled and washed with acetone and water. The resulting polymer was dried in an air oven at 120°C. The polymer had a Tg of 183°C, a melt viscosity at 400°C, 1000sec^{-1} of 0.78 kNsm^{-2} and an inherent viscosity (IV) 0.40 (measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84g.cm^{-3}, the solution containing 0.1g of polymer/100cm^3).

Example 16b

The above polymerisation procedure was followed except dried sodium carbonate (42.44g, 0.4 mole) and dried potassium carbonate (1.11g, 0.008 mole) was replaced by dried sodium carbonate only (43.24g, 0.408 mole). The polymer had a Tg of 183°C and a melt viscosity at 400°C, 1000sec^{-1} of 0.43 kNsm^{-2}

Examples 17 and 18

The polymerisation procedure of Example 16 was followed, except that copolymers were prepared by varying the mole ratios of the hydroxy-containing reactants, with the sum of the number of moles of the aforesaid equalling the number of moles of 4,4'-difluorobenzophenone. A summary of the mole ratios and the MV are detailed in the table below.

Example No	4,4'-dihydroxybiphenyl : 4,4'-dihydroxydiphenyl-sulphone	MV(kNsm^{-2})
17	1:2	0.67
18	1:3	0.72

Example 19

A 700ml flanged flask fitted with a ground glass Quickfit lid, stirrer/stirrer guide, nitrogen inlet and outlet was charged with 4,4'-dichlorodiphenylsulphone (104.25g, 0.36 mole), 4,4'-dihydroxydiphenylsulphone (6.75g, 0.27 mole), 4,4'-dihydroxybiphenyl (16.74g, 0.09 mole) and diphenysulphone (245g) and purged with nitrogen for at least 1 hour. The contents were then heated under a nitrogen blanket to between 140 and 145°C to form an almost colourless solution. While maintaining a nitrogen blanket potassium carbonates (50.76g, 0.37 mole) was added. The temperature was raised to 180°C, held for 0.5 hours, raised to 205°C, held for 1 hour, raised to 225°C, held for 2 hours, raised to 265°C, held for 0.5 hours, raised to 280°C and held for 2 hours.

The reaction mixture was allowed to cool, milled and washed with acetone/methanol (30/70) and water. The resulting polymer was dried in an air oven at 120°C.

Example 20 - Sulphonation of Polymers of Examples 11 to 19

The polymers of Examples 11 to 19 were sulphonated by stirring each polymer in 98% sulphuric acid (3.84g polymer/100g sulphuric acid) for 21 hours at 50°C. Thereafter, the reaction solution was allowed to drip into stirred deionised water. Sulphonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. In general, ^1H nmr in DMSO-d6 confirmed that 100 mole% of the biphenyl units had

sulphonated, giving one sulphonic acid group, ortho to the ether linkage, on each of the two aromatic rings comprising the biphenyl unit. For examples 13 to 15, 100% sulphonation of -O-Ph-Ph-O- moieties was confirmed by converting the sulphonated ionomer from the H^+ form to Na^+ form, by reacting 0.5g of the dry sulphonated copolymer with an aqueous solution of NaOH (2.5g NaOH/200ml water) at 60-65°C for 2 hours then washing the product with water and drying at 60°C, followed by sodium analysis.

Example 21 - Membrane Fabrication

Membranes were produced from selected polymers of Examples 11 to 19 after sulphonation as described in Example 20 by dissolving respective polymers in N-methylpyrrolidone (NMP) (15% wt/v). The homogeneous solutions were cast onto clean glass plates and then drawn down to give 300 micron films, using a stainless steel Gardner Knife. Evaporation at 100°C under vacuum for 24 hours produced membranes of mean thickness 40 microns.

Example 22 - Water-uptake of the Membranes

5cm x 5cm x 40 microns samples of membranes of Example 20 were immersed in deionized water (500ml) for 3 days, dried quickly with lint-free paper to remove surface water and weighed, dried in an oven at 50°C for 1 day, allowed to cool to ambient temperature in a desiccator then weighed quickly.

The water uptake was measured as follows, with the results being provided in the table below. "Equivalent

weight" is defined as the weight of polymer containing unit weight of replaceable acidic hydrogen.

$$\% \text{ Water Up-take} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

Membrane - prepared from sulphonated polymer of Example No:	Equivalent Weight	% Water Up-take
12	360	136.4
16a	476	61.5
17	690	30.5
18	904	21.9
19	976	21.6

Example 23 - Performance of membranes in a Polymer Electrolyte Membrane Fuel Cell

The membranes prepared from sulphonated polymers of Examples 19 and 17 were installed in a Standard PEMFC single cell test module and polarisation date was generated and compared to Nafion 115, a leading commercially-available membrane. The current densities obtained at 0.8V were 0.26 and 0.42Acm^{-2} for the Example 19 and 17 polymers respectively, compared to 0.12 Acm^{-2} for Nafion 115.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this

specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

1/1

Schematic of
Polymer Electrolyte Membrane Fuel Cell

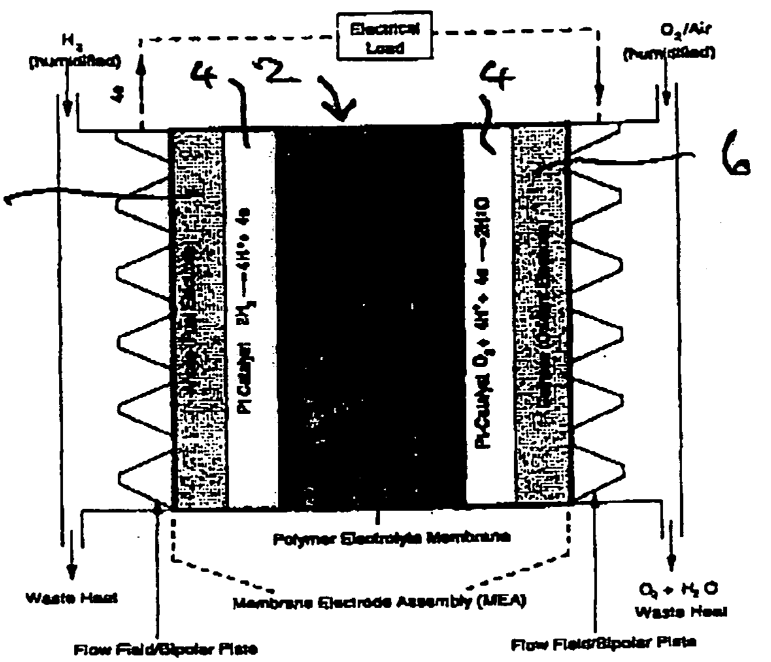


Fig 1

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Appleyard Lees